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NANOSCALE METAMATERIAL ENERGY CONVERSION DEVICES

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Abstract:

There is a general consensus among scientists and engineers that oil, gas, uranium and coal reserves will deplete by 2045-2050, 2060-2070, 2085-2095 and 2150. Post hydrocarbon era is likely to start from 2050 reaching to its climax by end of this century. There seemed to be no alternative to looming long emergency but recent developments in evanescent wave water splitting, carbon dioxide to carbon monoxide conversion and artificial photosynthesis techniques appear to hold the key to harness energy crisis. Fundamental advances in nanotechnology inspired energy conversion and storage devices can overcome energy predicament. Discoveries like nanoelectrolytes and nanophotoelectrodes for lithium batteries, fuel cells, photo-hydrolysis and supercapacitors can harvest as well as store energy. Metamaterials have potential capability to convert noise, infrared, visible light and ultraviolet into electricity. Optical antennas (Optenna), nano antenna (Nantenna) and rectifying antenna (Rectenna) are under fast development process to convert sunlight directly into electricity. This paper reviews recent advances in nanostructures gratings and antennas harvesting noise, heat and sunlight.

Keywords: Nanotechnology, Metamaterials, Optical antenna, Gratings, Energy crisis.

1. Introduction

Nanotechnology refers to application of scientific knowledge to control and utilize matter at the nanometer scale (1-100nm). Diffraction limits the confinement of propagating radiation to nearly half a wavelength which lies outside the nanotechnology scale range. Nanoscale metamaterials have the capability to interact with radio, microwave, terahertz, infrared, and visible light radiations. Metamaterials are artificially engineered materials having properties usually not exhibited by natural materials. Natural things occur in sizes much smaller than nanotechnology range but they do not occur so as to act as metamaterials. Matter consists of atoms, molecules and ions in nature. Atoms radii ranges from 32 pm (He) to 225 pm (Cs). Positive ions after loosing electron (s) shrink in size. Li (123pm) and Na (157pm) atoms covalent radii reduce to 68pm (Li^{1+}) and 95pm (Na^{1+}). Negative ions after getting electrons balloon in size. Br (99pm) and F (64pm) swell to 181 (Br^{1-}) and 136pm (F^{1-}). Bond length of hydrogen (smallest) molecule is 74pm. Organic materials molecules occur in few to several dozens angstroms sizes. Most molecules are too small to be seen by naked eye but DNA macro and polymer supramolecules occur in macroscopic sizes. Atoms (pm), molecules (1nm), cell membrane (10nm), viruses (100nm), bacteria (1μm), organelles (<10μm), and cells (<100μm) occur in very small sizes. Material scientists identify these tiny entities using electron (SEM), scanning tunneling (STM) and atomic force microscopes (AFM). STM can view surface down to atom level using quantum tunneling principle and AFM can identify down to sub-nanometer resolution in 3D using time of flight mass spectrometry.

A human hair width is about 1 million carbon atoms and a drop of water contains 2 sextillion water molecules. There is say “If an apple were magnified to the size of the earth, then the atoms in the apple would be approximately the size of the original apple” [Feynman, 1995]. New Scientist in 2004 claimed a need of heaven size equipment to measure smallest length but Lund University of Sweden recorded electron movie around the nucleus available on You Tube. Electron takes about 150as to circle around an atom. It takes attosecond to zeptosecond laser pulses to measure femtometer dimensions. Superposition of quantum states drives the motion on atomic and sub-atomic scales. Ultra-short laser pulses not only help measuring ultra-fine dimensions of structures [Hentschel, 2001] but also assist to artificially create them by direct writing [Vladimir, 2006]. Ultrafine periodic structures may also be generated by holographic techniques [Michael, 2001]. Smallness and bigness of thing in universe beyond Plank’s limits is well documented in literature [Khan, 2008]. The fact of the matter is we neither know the extent of smallness nor the level of largeness in universe. We try to see sky with naked eye our vision tunnels through blue horizon and telescopes (Hubble) take us just further a few billion times deeper without grasping any clue of ultimate time space curve. Keeping in mind the structure of a wall it appears as if it is necessary to build the universe with continuously decreasing size entities to make the whole. Standard model of physics concludes the matter consists of six flavors of quarks and six types of leptons bounded all together by gravity (gravitons), electromagnetism (photons), electroweak and strong forces (gluons). It is hard to visualize the constituents of sub-atomic particles.

Scientists and engineers have to some extent harnessed gravity (hydel power plants), strong forces (nuclear fission) and some regions of electromagnetic spectrum (solar cells). Nuclear fusion and optical antennas (Optenna) are under hot pursuit for energy security in post hydrocarbon era. Living science experts are working on light harvesting complexes for use in artificial photosynthesis whereas material scientists are developing nanoscale metamaterial gratings to increase solar cell efficiency. Electrical engineers and physicists are working on optical antennas to harvest light like electromagnetic radiations. Radio and microwave aerials can resonantly capture mm to meters size radiations. Sub-millimeter and micrometer size waves of terahertz and infrared radiations use metamaterials to fabricate resonant circuits. Although, extensive research has been carried out to explore materials [Daniel, 2005] and methods but no optical antenna is available in market to date. Vision of nanostructure antennas (Nantenna) can convert light directly to electricity. Rectifying antenna (Rectenna) progress is currently limited by high frequency THz diodes. Optenna nanostructures can capture light as well as improve lighting efficiency especially for organic light emitting diodes (OLED) in which 25% excitons are made in singlet and 75% in triplet states. Grating nanostructures act like antenna to enhance absorption efficiency. Perforated electrodes show a factor seven improvement. These perforations act as antenna allowing plasmon modes to couple to propagating radiation [[Palash, 2009]. Antenna enhances interaction between the emitter or absorber and the radiation field therefore it can be used to control the light-matter interaction. Simple deposition of over 100nm silver particles on thin film silicon-on-insulator cells increases 16-fold absorption [Pillai, 2007].

2. Metamaterials Science

Metamaterials possess physical properties not observed in natural materials. Natural materials may be artificially configured to form metamaterials having capability to extend properties of natural materials. Metamaterial paradigm may encompass nanocomposites, smart materials and metamorphose networks. Metamaterials come in nano (photonics), mm (microwaves) and meter (acoustics) scale sizes. Metamaterial size has to be a few times shorter than the interacting wavelengths. This condition is often taken as sine qua non requirement for the metamaterials [Ari, 2007]. Metamaterials can interact with optical, infrared, radio as well as

acoustic waves to increase solar absorption, conceal hot spots, camouflage ground and aerial vehicles or silence the noise. Metamaterials were envisioned about 50 years ago but active research started in 2000s. As metallic conductors resist to the flow of DC or AC currents in wires, the matter and atmosphere opposes the flow of electric and magnetic fields. Radio waves propagating through homogeneous dielectric medium face impedance given by

$$\eta = \pm\sqrt{\mu / \varepsilon} \tag{1}$$

Light waves propagating through dielectric medium encounter refractive index (n) given by

$$n = \pm\sqrt{\varepsilon\mu} \tag{2}$$

Where ε and μ are dielectric medium permittivity and permeability respectively. Complex values of parameters ε and μ have generally positive magnitude for all naturally occurring materials except few at specific wavelengths or in artificially configured metalmaterials. Victor Veselago in 1967 envisioned the possibility of extraordinary refraction occurring with negative refractive index in Maxwell equations for negative values of permittivity or permeability. A metamaterial must have negative ε and μ (electromagnetic waves and negative ρ or β (acoustic waves). If both ε and μ become negative then product $\varepsilon\mu$ becomes positive therefore under such situations negative square root of (2) must be taken as materials exhibit metamaterial properties. However, material science research will eventually show someday the existence of conditions to take positive square root for materials not exhibiting metamaterial properties despite having negative ε and μ. Chiral metamaterials (metallic helices for radar beam absorption) refractive index for left and right hand polarizations is given by

$$n = \sqrt{\varepsilon\mu} \pm k \tag{3}$$

Negative index will occur only for one polarization for k > $\sqrt{\varepsilon\mu}$. This eliminates either or both ε and μ be negative for overall negative refractive index condition [Zouhdi, 2008]. Fixed frequency constraints can be overcome by frequency selective surface (FSS) based metamaterials. Refractive index of optical materials changes under high intensities of laser pulses that can effectively be overcome by nonlinear optical metamaterials. Natural materials through artificial configurations may be made to achieve negative refractive index for radio, microwave, IR and optical frequencies. Electromagnetic metamaterials can offer resonant absorption of radar and light waves, super resolution as well as flat slab focusing properties.

Acoustic metamaterials for effective mass density (ρ) and bulk modulus (β) can offer negative refractive index to certain bands of sound waves given by

$$n = \sqrt{\rho / \beta} \tag{4}$$

No natural material exhibits negative ρ or β but the same may be achieved through resonant frequencies of artificially fabricated metamaterials. Negative ρ or β situation is achieved at certain sound frequencies when medium expands experiencing compression ($-\beta$) and accelerates to left when being pushed to right ($-\rho$) [Krowne, 2007]. When negative refractive indices are achieved in metamaterials the light, microwaves and sound waves encounter Poynting vector (**s**) opposite to direction of wave vector (**k**).

Like photonic crystals sonic crystals can also exhibit negative refractive index to reflect seismic wave, noise cancellation in busy places and sonar blinding of submarines. Infrasonic frequencies range from 0.001 to 20Hz, audible from 20Hz to 20 kHz and ultrasonic from 20 kHz to 1GHz. Acoustic metamaterials may be made in solid, liquid and gas phase forms to deal with

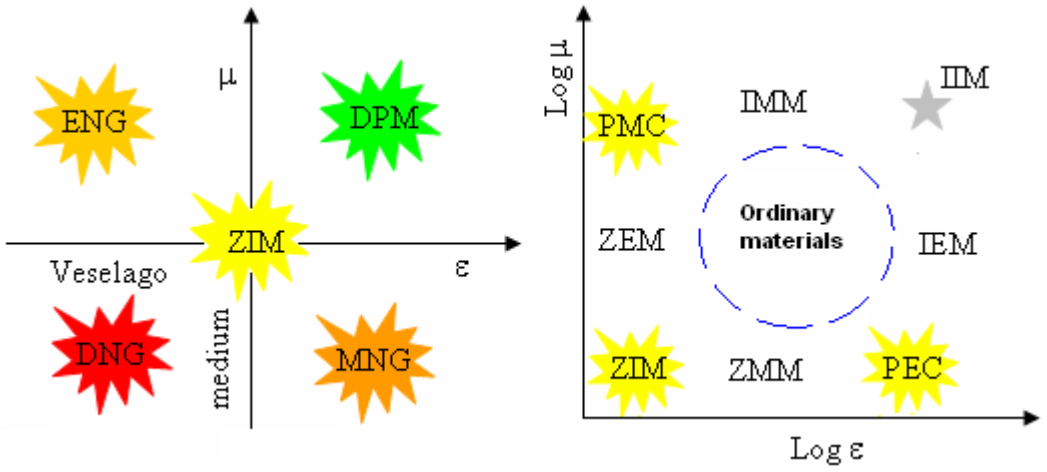
elastic waves. Optical nonlinearity dictates possibility of intense sound waves nonlinear behavior in acoustic materials. High intensity and velocity subsonic (<270m/s), supersonic (400-1710m/s) and hyper supersonic (1710-3415m/s) sound waves have Mach numbers <1 to >1 for subsonic and supersonic (sound barrier) waves which can probably change the effective refractive index of sound wave medium in nonlinear manner necessitating need for nonlinear acoustic metamaterials. Acoustic metamaterials can be an effective shield to absorb noise frequencies but can not absorb jet take off noise [Smith, 2000]. Wavelengths associated with electromagnetic waves may range from 1fm to several thousands of kilometers. Ultimate limits of wavelength are bounded by Planks limit (10^{-35}m) and size of universe. Ultimate phonon-photon interactions through plasmon polariton based evanescent waves may bring about new revelations.

Materials science and technology from microelectronics, thin films, electrochemistry, bio sciences and nanotechnology have gradually matured over time. These technologies have been explored continuously to develop sustainable energy systems. Solar thermal, photovoltaic, solar hydrogen, solar satellites, wind, hydro and even biomass are all sun based energy systems [Zach, 2006]. Nuclear fusion, geothermal, gravitational and extraterrestrial feedstocks are renewable energy resources. Oil, gas, coal, unconventional fossil fuels and nuclear fission are definite resources which are likely to deplete sooner or later. Solar and renewable energy resources may be stored in form of water dams, super giro, pneumatic, hydrogen, batteries and superconductors. Energy storage systems employ combustion engines, turbines, fuel cells, MHD generators, thermo, photo and piezoelectric materials to convert energy from one phase into others. We use energy for residential, transport and industrial applications. Use of energy causes increased amount of greenhouse gases in air that requires catalysts to clean the air. Solar cells employ nanostructures to convert sunlight into electricity. Solar thermal systems may employ metamaterials to convert infrared heat into electricity. Photosynthesis antenna system inspired nanostructures may convert electromagnetic field energy into electricity using carbon nanotubes, zeolites and metallic nanoparticles [Zhdanov, 2004]. Semiconductor clusters, nanocrystals and quantum dots have an established history in contemporary science and technology [Alivisatos, 2002]. Nanoscale metamaterials have even brighter prospect for developing energy converting devices as noise (infrasonics), heat (IR), phonons and photons to electricity conversion applications.

Visible light photons below 500nm wavelengths have enough energy to break water into hydrogen and oxygen molecules. Photochemical water splitting systems suffer from fast electron hole recombination. Noble metal particles < 5nm sizes permit charge separation between semiconductor and metal interface which can enhance splitting efficiency. Carbon and titania nanotubes and hematite films can increase water splitting efficiency. Hot electron attachment not only allows water photo-splitting but also byproducts of CH_4 and CO fuels. Nanostructures can minimize time and distances over which charges survive and transported after excitation like ATP to ADP conversion in living systems. Nanoparticles have shorter distances between core and shell. The core is optimized for photoexcitation to generate electron hole pairs and shell is optimized for hot electron induced reactions increasing electron hole pairs capture cross-section. Improvement in charge separation increases conversion efficiency. It may be achieved by deposition of noble metal nanoparticles on semiconductor support, quantum confinement in semiconductor clusters and photocatalytic nanodiodes [Abrams, 2005]. Idea of plasmonic nanoparticle evanescent fields may also be considered for solar water splitting. Nanoparticles below 100nm size behave differently compared to bulk materials. Kinetic effects are dominant at 10 to 100nm but electronic effects also appear at 1 to 10nm sizes. Electronic reactivity effects prevail at 100pm to 1 nm sizes beyond which measurements go beyond spatio-temporal resolution. It is advisable to fabricate, characterize and test to dig

deeper in nanotechnology. Materials science and technology plays central role in energy and environment technology.

Metamaterials have been fabricated for radio, microwave, IR, terahertz, optical and UV as well as sound waves. Natural and artificially fabricated materials types range from doubly positive (DPS), doubly negative (DNG), epsilon negative (ENG) and Mu negative (MNG) materials as shown in Fig.1 (a) and perfect electric conductors (PEC), perfect magnetic conductors (PMC), zero electric (ZEM), zero magnetic (ZMM), infinite electric (IEM), infinite magnetic (IMM) and infinite index materials (IIM) as shown in Fig.1 (b) on log scale.



a. Normal value materials in $\varepsilon\mu$ plane b. Extreme value materials in $\varepsilon\mu$ plane

Figure 1: Classification of negative, zero, positive and extreme value materials

Ferroelectrics have low $+\mu_r$ and high $+\varepsilon_r$ and ferromagnetics high $+\mu_r$ and low $+\varepsilon_r$. Right handed media possess average $+\mu_r$ and $+\varepsilon_r$ values whereas left handed media do have average $-\mu_r$ and $-\varepsilon_r$ values. Ionosphere has low $+\mu_r$ and high $-\varepsilon_r$ values [Lippens, 2008]. Magnitudes of μ and ε in perfect electric conductors (superconductors) are zero and infinity whereas opposite in perfect magnetic conductors. Materials bearing extreme values may be used in increasing antenna directivity, cloaking and squeezing optical energy [Ari, 2007]. Discussion of various negative index materials is reported in recent literature [Scott, 2011]. Scientists hold the whole in more than simple sum of individual sums. A synergic approach may lead to emergence and evolution theory of complex adaptive systems.

3. Split Ring Resonators (SRR)

A single cell SRR has a pair of enclosed loops with splits in them at opposite ends. These rings are made of non-magnetic metals and have a gap between them. These loops may be concentric, squared and gapped. The gap helps loop to resonate with λ much larger than loop. If loop is closed then circulating current in loop will produce opposite flux. Gap capacitance reduces resonant frequency. It also increases quality factor reducing radiative losses. SRR should have inner radius 30 to 40 nm for visible light. Direct laser beam writing and electron beam lithographic techniques can be used to produce a few tens nm sized structures. Negative permeability (μ), permittivity (ε) and refractive index (n) materials have been found in radio, microwave, terahertz, infrared and visible ranges. Split ring resonator may take form of two square rings, rectangular squares, parallel omega structures (vertical), vertical S shapes, two layers multiple spiral, open split ring and open complementary split ring resonators. Photonic

metamaterials interact with terahertz, infrared and visible waves. Metamaterials manipulate loss components of permeability (μ), permittivity (ε) and refractive index (n) materials which cause attenuation. Real parts relate to wave propagation not loss factor which can be engineered to cause high losses.

Radio detection and ranging (RADAR), sound detection and ranging (SODAR), sound navigation and ranging (SONAR) and cameras can be blinded by fixing metamaterial on surface of aircrafts, submarines and battle field tanks as well as soldiers. Radars use radio and microwave beams, sonar use 192 kHz (shallow) or 50 kHz (deep) acoustic beams which can be absorbed by metamaterial structures. Aerial vehicles and tanks use split-ring resonators to absorb radar beams. A split-ring resonator act like parallel LC resonant electric circuits shown in Fig.2

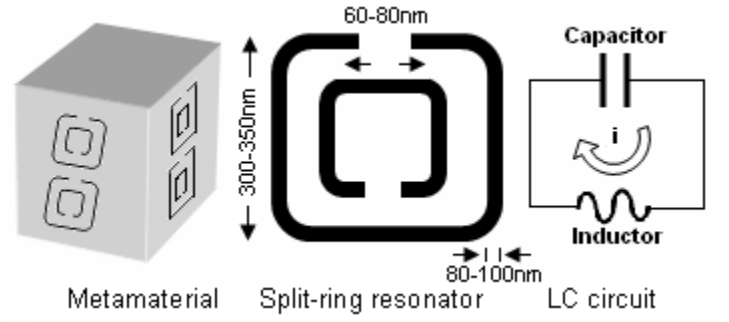


Figure 2: Principle of split-ring resonator based metamaterial

Outer or inner ring air gap (capacitor) and metallic structure (inductor) acts as LC series resonant circuit. Assuming a DC battery driving the LC circuit the voltage equation becomes

$$V_B = V_L + V_C \quad (5)$$

$$V_B = L\frac{di(t)}{dt} + \frac{1}{C}\int i(t)dt \quad (6)$$

Differentiating leads to $dV_B/dt = 0$ on LHS in (6)

$$0 = L\frac{d^2i(t)}{dt^2} + \frac{i(t)}{C} \quad (7)$$

Rearranging (7) gives

$$\frac{d^2i(t)}{dt^2} + \frac{1}{LC}i(t) = 0 \quad (8)$$

At resonance $\omega^2 = LC$ therefore

$$\frac{d^2i(t)}{dt^2} + \omega^2 i(t) = 0 \quad (9)$$

Laplace transformation gives $s^2 + \omega^2 = 0$ or $s = \pm j\omega$. General solution of (9) in time domain gives following expression for resonant current in LC circuit

$$i(t) = Ae^{j\omega t} + Be^{-j\omega t} \quad (10)$$

For A =B equation (10) reduces to 2Acosωt = 0 (for ωt = 0) rendering $d^2i(t)/dt^2 = 0$. LC circuit impedance is zero at $\omega^2LC < 1$ LC and infinite at $\omega^2LC > 1$ LC at which the circuit acts as band pass and band stop filter. Like LC circuit the metamaterials can absorb or transmit about (100%) light, radar beam and sonar signals. A metamaterial LC circuit may consist of single, double, triple and quadruple air gaped ring resonators shown in Fig. 2

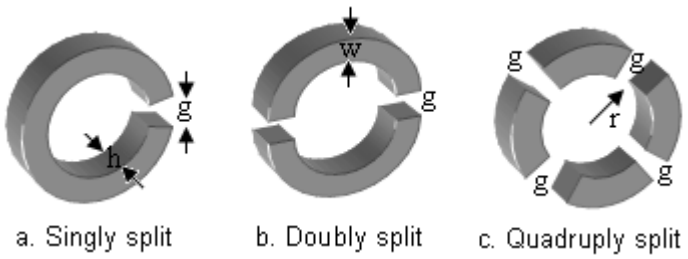


Figure 2: Geometries of singly, doubly and quadruply split resonator

Metallic resistance, kinetic and magnetic inductances, gap and surface capacitances of singly split ring resonator are given by [Sydoruk, 2009; Grover, 1981]

$$R = \frac{(2\pi r - g) f_c^{'}}{S\omega_p^2 \varepsilon_o} \tag{11}$$

$$L_{kin} = \frac{(2\pi r - g)}{S\omega_p^2 \varepsilon_o} \tag{12}$$

$$L_{mag} = \mu_o r\left[\log\frac{8r}{h+w} - \frac{1}{2}\right] \tag{13}$$

$$C_{gap} = \varepsilon_o \frac{hw}{g} + \varepsilon_o (h + g + w) \tag{14}$$

$$C_{surf} = \frac{2\varepsilon_o (h+w)}{\pi}\log\frac{4r}{g} \tag{15}$$

Where effective electron collision frequency $f_c^{'}$ for mean free path (l_e), ω_p is plasma frequency and Fermi velocity (v_F) is given by

$$f_c^{'} = v_F\left(\frac{1}{l_e} + \frac{A}{2w} + \frac{A}{2h}\right) \tag{16}$$

Where the parameter A is a close to unity, $f_c^o << \omega/2\pi \approx 121.9$ THz resonating at ω_o

$$\omega_o = \frac{1}{\sqrt{(L_{mag} + L_{kin})(C_{gap} + C_{surf})}} \tag{17}$$

At magnetic saturation L_{mag} becomes zero

$$\omega_s = \frac{1}{\sqrt{(L_{kin})(C_{gap} + C_{surf})}} \tag{18}$$

In case of doubly split ring resonators all parameters remain same except surface capacitance

$$C_{surf}^{2gap} = \frac{2\varepsilon_o(h+w)}{\pi}\log\frac{2r}{g} \tag{19}$$

$$C_{total}^{2gap} = \frac{C_{gap} + C_{surf}^{2gap}}{2} \tag{20}$$

In case of quadruply split ring resonators all parameters remain same except surface capacitance [Delgado, 2009]

$$C_{surf}^{4gap} = \frac{2\varepsilon_o(h+w)}{\pi}\log\frac{r}{g} \tag{21}$$

$$C_{total}^{4gap} = \frac{C_{gap} + C_{surf}^{4gap}}{4} \tag{22}$$

Design of higher order open split ring resonator for T and Pi circuits for 7th order band pass Chebyshev filter are described elsewhere [Miguel, 2011]. Double negative metamaterial sensors based on microring resonance are described elsewhere [Jing, 2011].

Split ring resonators (SRR) for millimeter waves at X-band (8-12 GHz) may be fabricated using printed circuit board (PCB) technology. SRR lateral dimensions have to be smaller than beam waist. A 1-cm SRR sample has typically 200μm diameter rings. Dimensions will shrink for higher frequency ranges. A 100 GHz wave has 3mm wavelength that corresponds to largest 300μm diameter ring. It means miniaturization factor SRR/wavelength i.e. 300/3000 = 1/10 is approximate guess that may vary in practice. In case of IR radiation (100 THz) the wavelength is 300nm that would require 30nm diameter SRR which behaves nonlinearly. Standard technology does not allow precise fabrications such a small sizes as SRR wire size has to be much smaller than 30nm. Reactive ion etching (RIE) technique is suitable down to 200nm beyond which inductively coupled plasma (ICP) etching may be considered [Lippens, 2008]. Definite fixed nanosize structures might not serve the purpose. Thermally tunable THz devices can span the whole of IR spectrum. Semiconductor's relative permittivity may be modified by changing temperature, external magnetic field, pumping light intensity or applied voltage [Zhu, 2011]. Complex permittivity (Drude model) may be expressed by

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_P}{\omega^2 + i\gamma\omega}$$

Where γ is damping factor and ω_p is plasma frequency given by

$$\omega_P = \sqrt{Ne^2/\varepsilon_o m^*}$$

Plasma frequency depends upon concentration of carriers density N and effective masses m^* of free carriers. Damping factor $\gamma = e/\mu m^*$ depends upon temperature. Carrier density N for InSb at temperature T is given by [Zhu, 2011]

$$N = 5.76\times10^{14} T^{3/2} \exp(-0.26/2k_B T)$$

A terahertz frequency unit cell SRR is shown in Fig.5 (a)

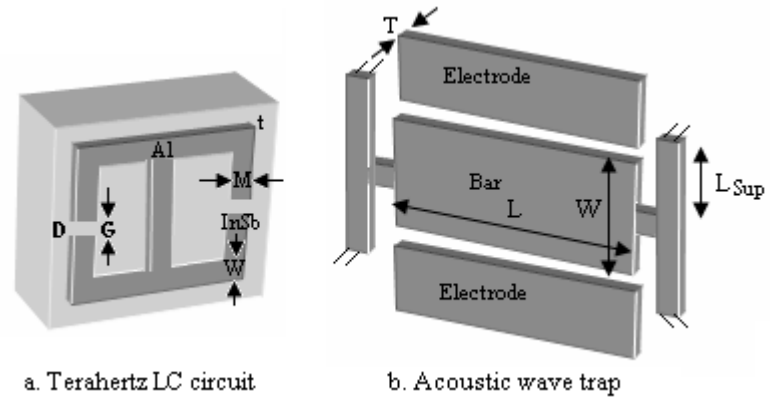


Figure 5: Unit cells of a. terahertz SRR and b. acoustic wave trap

Inductance, capacitance and resonant frequency of terahertz LC circuit (Fig.5a) may be calculated by formulae reported in literature [Jeppesen, 2009]

$$L = \frac{\mu_o D^2}{t}$$

$$C = \frac{\varepsilon_o \varepsilon_{eff} tW}{G}$$

$$\omega_o = \alpha \frac{c}{D} \sqrt{\frac{G}{W\varepsilon_{eff}}}$$

Acoustic metamaterials may be engineered to produce phononic band gaps for wave trapping. Bar wave trap (Fig.5b) vibration modes are given by [Rottenberg, 2011].

$$f_{bar} = \frac{1}{2} v_{sound}(\varsigma, \rho, \nu) \sqrt{\frac{l^2}{W^2} + \frac{m^2}{L^2} + \frac{n^2}{T^2}}$$

where ζ is Young's modulus, integers l, m, n are mode numbers.

3D acoustic cloaking has already been demonstrated in literature [Chen, 2009]. Noise can be cancelled by feeding back the error by microphone between noise source and noise canceling speakers to realize a noise free environment [Gehardus, 1986]. Multiple noise sources may be cancelled by placing microphones near all noise sources and one near real speech source. A multi-reference adaptive noise canceller (MRANC) reported elsewhere [Easfy, 1988]. Low frequency bass sounds often sneak through thick walls which can be reflected or even absorbed by foam allowing sound proof rooms [Dupont, 2011].

Like optical, electrostatic and magnetic lenses acoustic lens may be realized by placing a metamaterial gas balloon medium between speaker (mouth) and receiver (ear). Idea of super lens has help improve resolution limits in image processing. Principle of invisibility and target shielding applications is illustrated in Fig.3

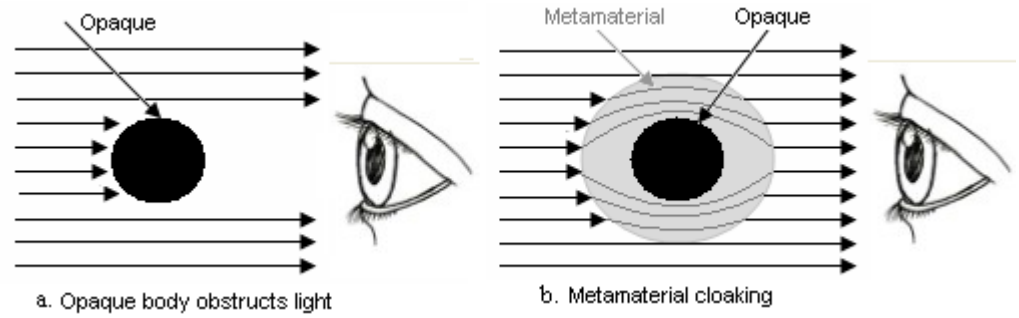


Figure 3: Principle of invisibility illustrated using metamaterials

Light wavelength is too small for which metamaterial structures have to be ten times smaller to deal with them. Idea of space-time cloaking by researchers in Imperial College London seems feasible [Clay, 2010]. Chinese claim to have developed artificial black hole in laboratory which emit heat in response to light trapping that naturally renders it attractive for solar cells [Stuart, 2009]. Metamaterials like darker than black are useful for solar thermal power generation and waste heat harvesting [Clay, 2011]. Cloaking may be done by scattering or cancellation by multiple thin layers and coordinate transformation using metamaterials in 2D structures [Wood, 2011]. Principle of 3D plasmonic cloaking at microwave was discussed elsewhere [David, 2011]. Metamaterials may be designed to absorb radiations in a wide range. Metamaterials consist of nanoscale structures whose lateral dimensions may be tuned by temperature, optical pumping, electric, and magnetic field changes. Metamaterials have successfully used to demonstrate filters, modulators, amplifiers and resonators. Reconfigurable metamaterials must have capability to change response to reflect, absorb or transmit the incoming radiation fields. Varactor diodes, semiconductor materials, barium strontium titanate thin films can tune elements. Control may be achieved through variation of permittivity and permeability so as to change the effective refractive index or impedance. It may be achieved by immersing metamaterial wire-grids in liquid crystals which change their characteristics by voltage. Frequency selective surface materials and artificial magnetic conductors appear good candidates.

4. Light Trapping Gratings

Light trapping on solar absorber surface may be carried out by antireflection coatings, optical switched coatings, Goos Hanchen shift layers and a range of binary and multiple complex grating structures in optical, infrared and microwave regimes [Maria, 2011]. Nano to micro scale metamaterials, artificial structured meta atoms, screens and carpets, cover sub-millimeter to optical parts of electromagnetic spectrum. Conventional chemical etching methods are limited to 500μm which may be extended well down to a few hundreds nanometers by lithographic methods. Direct laser writing on hybrid sol-gel photosensitive materials has potential to create 3D micro optical components with sub-100nm resolutions where the nanomaterials exhibit nonlinear behavior. Femtosecond lasers have been reported to fabricate 75nm pits on copper film, 15nm width gratings on amorphous silica, 65nm wires on urethane acrylate resin, 40—70nm hillocks on glass, 30nm voids on TeO_2, 20nm strips on SiO_2, 100nm layer on Lithium niobate, 50-100nm ripples on CVD diamond and 20-40nm nanorods on AAO matrix [Li, 2011]. Machining processes have resolutions above 1μm. It is limited by optical diffraction limit ($d = \lambda/2n\sin\alpha$). Nanostructures may be fabricated using beam scanning at 50μm/s speed with laser power of 20mW. It corresponds to 0.125 to 0.3 nJ per pulse energies at repetition rate of 80MHz and 0.5 to 1 TW/cm^2 intensities at focal spot allowing 200 to 600nm lateral and longitudinal resolution of 3D structures [Mangirdas, 2011]. Nanoscale particle layers can help control intensity, phase and polarization of microwaves and optical systems.

Traditional antireflection (AR) thin film coatings on solar cell surface enhance light absorption capacity. An AR coating may consist of multiple layers of different step refractive indice materials. AR coatings with triangular and parabolic refractive indice profiles are well known. Coupled wave analysis shows that quadratic refractive index profile AR coatings can significantly enhance light absorption. Application of different profiles refractive indice materials has been found to reduce reflectivity from 0.8 to 1.9% over 300 to 1100 nm range. Reflectivity of AR coating may be given by

$$R = \frac{1}{2}\sum_{m=-\infty}^{+\infty}(DE_{m-TE} + DE_{m-TM}) \tag{11}$$

where the parameters $DE_{m\text{-}TE}$ and $DE_{m\text{-}TM}$ are diffraction efficiencies at mth order of TE and TM polarizations. Average reflectivity for total solar illumination wavelengths, incidence angles and both TE and TM polarizations may be given by [Li, 2011]

$$R_{Ave} = \frac{1}{2}\frac{\int_{300}^{1100nm}\int_{0}^{\pi/2}[R_{TE}(\lambda,\theta)N_{Photon}(\lambda) + R_{TM}(\lambda,\theta)N_{Photon}(\lambda)]d\theta d\lambda}{\int_{300nm}^{1100nm}N_{Photons}(\lambda)d\lambda} \tag{12}$$

A grating structure may enhance light trapping by increasing transmission or back reflection. Texturing the solar cell surface in combination with anti-reflection coating increases light absorption [Hava, 2000]. Lamellae and V-grooved gratings with over layers may be used to increase absorption of light by solar cell. Periodic structures may have different individual absorption efficiencies but certainly more than simple flat surface Si-SiO_2 layer cells. Solar irradiance is maximum (0.15 w/cm^2/μm) at 500nm. Application of grating structure may reduce18% reflection at 500nm to 8% at 600 to 550nm at 45°l incidence. In case of normal incidence using trackers the angular reflectance may be 2 to 3%. It involves refractive diffraction phenomenon at $\lambda \geq \Lambda$ and theoretically allows reflection from 1 to 4% increasing solar cell efficiency. Examples of various gratings are shown in Fig.4.

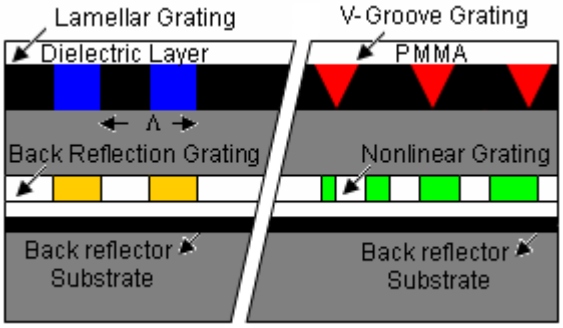


Figure 4: Solar cell linear and nonlinear gratings

Use of back reflection grating structure on base of solar cell increases light trapping. Assuming $4n^2$ light paths the internal quantum efficiency of solar cell, with back reflecting grating structures, increases to 73% (14% higher) that may further increase to 81% (37% higher) for longer diffusion lengths [Yang, 2011]. Solar cells absorb weakly a fraction of solar spectrum that may be enhanced using periodic structures. Light trapping is commonly increased by rough and geometric texturing of front and rear face of the solar cell. The bi-periodic binary back reflecting diffraction gratings may take the form of hills and wells on bottom of substrate. Coherence

length of solar spectrum is very small (≈1μm) so it is advisable to use relatively thicker gratings. Theoretical optical path length caused by lambertian surface is $4n_{cell}^2$ [Yablonovich, 1982]. Light absorption may be enhanced compared to lambertian limit if the light capturing mechanism is angular selective. This may be achieved by a cone of semi-angle 0.26° oriented normal to surface having solar disc inside it using sun tracker within accuracy of 1°. Maximum light capturing occurs at λ/Λ is just above the value at which diffracted cones begin to escape the cell. Higher absorption is possible at $\lambda/\Lambda < 0.9$ which can only be achieved by grating profiles restricting coupling between escaping and confined orders that may be expressed by $0.9<\lambda/\Lambda<1.1$. For $\lambda/\Lambda = 1$ the spectral reflection and transmission minima and maxima for hexagonal arrays of elliptical wells and towers are given by [Mellor, 2011]

$$(d/\Lambda)_{r-} = \frac{m-1/2}{2n_{cell}} \qquad (d/\Lambda)_{r+} = \frac{m}{2n_{cell}}$$

$$(d/\Lambda)_{t-} = \frac{m-1/2}{n_{cell}-n_{clad}} \qquad (d/\Lambda)_{t+} = \frac{m}{n_{cell}-n_{clad}}$$

A recent study of sub-wavelength apertures holey metal (metamaterial) has shown that square type holes exhibit better extraordinary transmission compared to circular holes. It leads to polarization and frequency selective devices [Miguel, 2011]. Perforated holes or slit arrays are believed to support surface plasmon polaritons responsible for enhancement of electromagnetic waves transmission. Extraordinary optical transmission through thin slits in thick metal is a well known phenomenon. It is based on collective plasmonic resonance of corrugated screen. Light (750nm) was found to tunnel through optical gratings successfully at 75° Brewster angle [Andrea, 2011]. For transmission resonances in plasmonic metallic gratings the magnetic field (**H**) must be polarized parallel to 100nm grating slits and electric field (**E**) along grating periodicity [D'Aguanno, 2011]. Absorption of light by extremely shallow 1, 2 and 3D metallic gratings is a metamaterial behavior [Evgeny, 2009]. Crossed gratings can absorb effectively unpolarized sunlight [Popov, 2008].

Complex nonlinear gratings structures provide the critical path to enhance solar cells light capturing capability. Complex tungsten gratings have been reported for thermo-photovoltaic (TPV) applications in 1.5kW combined heat and power (CHP) applications. Superimposed tungsten gratings act as efficient thermal radiator. Combination of thermal emitter and PV diode can convert heat (IR) at 900 to 1300°C to electricity via photons. TPV efficiency is limited to just 12.3% but it may be enhanced using 1D, 2D, 3D micro and nanostructures. General 1D deep grating structures and 2D micro resonance cavities enhance resonance modes. Gratings excite surface electromagnetic waves or polaritons for coherent thermal emission. Cavity resonance modes and surface polaritons produce thermal emission source. Solar cells convert light into electricity when photon wavelength is shorter than the band gap wavelength. Longer wavelengths produce only heat that may be used to cause emission at wavelength of interest. TPV radiators should have emission wavelength corresponding the absorption band of solar cells. Some researchers fabricated 2D tungsten grating achieving 70% emittance at 1.6μm and others fabricated 3D tungsten grating photonic crystals with enhanced absorption and emission wavelengths from 1.5 to 1.9μm [Chen, 2007]. Interaction of two binary gratings with periodicities Λ_x and Λ_y produces a complex nonlinear structure supporting experimentally noted five modes with periodicities Λ_1 to Λ_5. Additional three gratings with periodicities Λ_2, Λ_3 and Λ_5 as shown in Fig.5

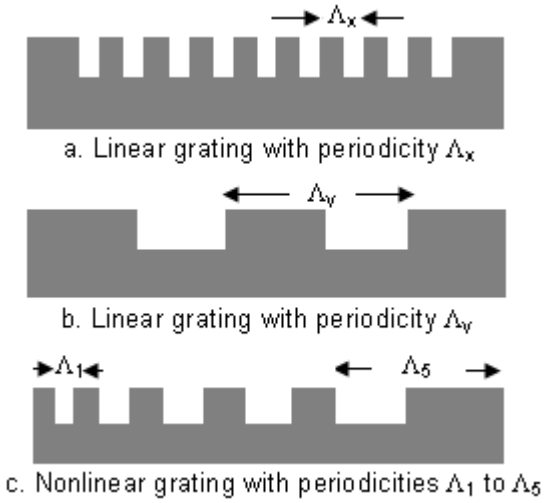


Figure 5: Nonlinear interaction of two gratings

Standard 600-1100nm solar spectrum is very poorly absorbed in single pass through less than 10μm thick silicon film. Conventional wafer based crystalline silicon solar cells have absorption thickness of about 300μm. Minority carriers diffusion length must be several times the material thickness that is bet met in thin film solar cells. Solar cell absorption thickness and carrier collection length oppose each other. Plasmonic structures can meet the both requirements. Sub-wavelength metallic nanoparticles can be deployed at front and back surfaces to scatter the light within cell body to increase the length of wafer based solar cells. A corrugated metallic film on back and front of thin photovoltaic absorbers couples sunlight into guided modes where light is converted to photo-carriers. This allows fabrication of ultra thin solar film solar cells. Surface plasmons are electronic charge density fluctuations at the interface between a conductor and a dielectric [Thomas, 2010].

When illuminated by optical field a dielectric material acts as RC circuit whereas metamaterial acts as RL circuit both having fringe capacitances given by [Andrea, 2011]

$$C = \frac{\pi a n \,\mathrm{Re}(\varepsilon)}{U(a,b,c)} \qquad L = \frac{U(a,b,c)}{-\omega^2 \pi a b \,\mathrm{Re}(\varepsilon)}$$

$$R = \frac{U(a,b,c)}{\omega \pi a b \,\mathrm{Im}(\varepsilon)} \qquad C_f = \frac{\varepsilon_o \pi a b (1 - L_z(0))}{L_z(0) U(a,b,c)}$$

Where L_z (0) is elliptical integral of illumination patch. Illuminated patches with $\varepsilon_L<0$ (metamaterials) and dark parts with $\varepsilon_C>0$ (dielectrics) may form series and parallel LC circuits. Different nanocircuits may be envisioned depending upon the orientation of nano spheres with respect to incident electric field as shown in Fig.6

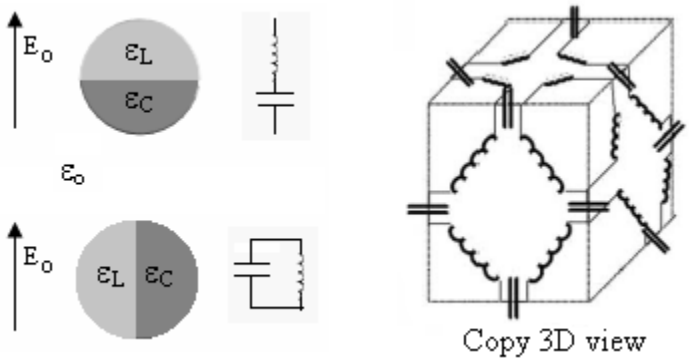


Figure 6: Nanospheres series and parallel circuits [Andrea, 2007]

A nanoscale annular array of apertures in thin silver films was reported for infrared regime. As RFID tags are powered with remote beam the nanoscale circuits may be powered by sunlight. Nano radio and nano robotics may be powered by such circuits [Andrea, 2007]. Such nanocircuit plasmonic structures are known as metactronics another term like plasmonics and spintronics. Design procedure for nanoscale metamaterials from terahertz to visible range are well documented in literature [Zhao, 2006]. Nanoscale light source laser and surface plasmon spaser are actively being pursued for nanophotonic applications.

Acoustic phononic crystal metamaterial at acoustic atom scale with negative bulk modulus and mass density exhibits negative refraction. Acoustic surface evanescent waves help achieve acoustic sub-wavelength imaging, enhanced transmission, dispersion, band gap, band edge states, slow light and super lens effects. Bragg and localized Mie scattering gives rise to dispersion in acoustic phononic crystal (APC) in fluid matrix and elastic phononic crystals (EPC) in elastic solid matrix. Phononic crystals may be used for sound insulation, shock proofing, slow wave effects, acoustic wave filtering and acoustic waveguides for collimation and directed beaming. Real materials have neither negative mass density nor negative elastic modulus. Artificially engineered APC and EPC may have their own resonant frequencies and counterintuitive features. The acoustic atoms have their intrinsic and inertial properties. Cylinders and spheres have potential to exhibit coherence. Air bubbles in water may exhibit mono or dipolar resonance at different acoustic frequencies using negative indices. Negative refractive index of an acoustic metamaterial may be given by

$$n = \sqrt{\beta_o \rho_e / \beta_e \rho_o}$$

Where β_o and ρ_o are reference and β_e and ρ_e are effective bulk modulus and effective densities respectively. Acoustic Helmholtz and sub-synchronous resonance phenomenon were noted long ago to impart backward power flow. Electric generator transfers power to acoustic mechanical vibrations caused by prime mover drive system. Negative group velocity is associated with coupling between two resonant acoustic modes like electromagnetically induced transparency. Bulk acoustic waves and elastic waves such as Lamb waves and Rayleigh waves in principle can be controlled by phononic and acoustic materials 2D structures on solid plate or surface of a solid allowing chip integration for signal processing and sensor applications. Antenna like tiny structures on moths and orthopods are natural examples of acoustic metamaterials. Miniaturization efforts may eventually end up in coupling between photon and phonons [Lu, 2009].

5. Light Harvesting Antennas

Optical antenna (Optenna) is a nanoscopic rectifying antenna which may convert sunlight into electricity. Theoretically antenna can absorb any radiation provided its size is optimized for its wavelength. IR optical antennas have been fabricated in asymmetric spiral, micro-strip dipole, square spiral and phased array metamaterial designs. Idaho National Laboratory has developed nano antenna (nantenna) capable of absorbing 3 to 15μm wavelength infrared radiations. Generally solar energy is distributed in UV (7%), visible (44%) and IR (48%) parts of its spectrum, however, 85% of solar energy is confined in 400nm to 1.6μm spectrum. A few patents claim direct light to electric power conversion using nantenna. Some individuals claim to have achieved resonant light absorption and rectification [Lin, 1996]. Optenna size has to be maximally comparable to light wavelength. A schematic diagram of an optical antenna is shown in Fig.7.

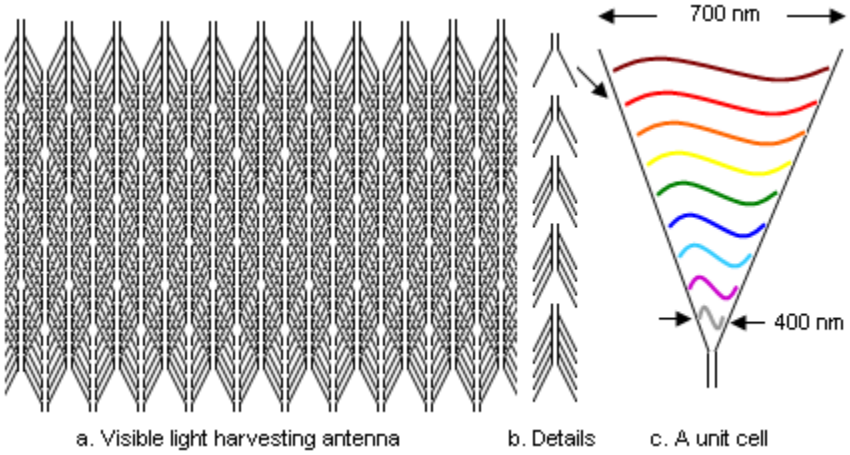


Figure 7: Schematic diagram of an optical antenna (optenna)

Optical rectifying antenna (Rectenna) design faces size, skin effect and diode constraints. Nanotechnology helps overcome size issues but skin effect due to circulating eddy currents increases resistance and so the power loss. Skin depth δ and resistance R for a wire of length L and diameter D are given by

$$\delta = \sqrt{\frac{2\rho}{\omega\mu}} \qquad\qquad R = \frac{L\rho}{\pi D\delta}$$

Copper and aluminum wires have skin depths of 0.65 and 0.80μm at 10GHz [Ramo, 1994]. Wire resistance is inversely proportional to skin depth. As skin depth drastically reduces therefore wire resistance increases. Litz wires reduce skin effect but not useful at THz. Rectenna needs a metal insulator metal (MIM) type diodes for 0.4 (190THz) to 1.6 (750THz) μm light wavelengths. Available p-n junction and Schottky diodes operate up to 5THz and MIM up to 150THz [Berland, 2009]. A semiconductor can not operate above 100GHz because of material limitations. Optical diodes are likely to confront 190 to 750THz speed, <1V voltage, 2-4×10^6 A/cm^2 current densities and 100°C temperature [Phiar, 2003]. MIM design may be augmented to incorporate metal double insulator metal (MIIM) structures. MIM or MIIM like Schottky diode is based on electron tunneling effect. Incident light on antenna causes electrons to move back and forth on antenna. To convert AC light waves into DC the circuit needs a high frequency diode.

6. Conclusions

Metamaterials for acoustics, microwave, infrared, terahertz and visible light fields is a sleight of hand rather than any transcendent material [Marie, 2011]. Darker than black metamaterial, can lead to efficient light collection in solar cells. Metamaterials are fabricated with metals which are perfect conductors of electromagnetic waves but not light. Search for microwave to visible light tunable metamaterials is an uphill task. Highly absorbing metamaterials are desired in solar applications. Metamaterials may help design intelligent window panes and blind designs effectively shielding hot spots and allowing sunlight entrance. Corrugated metamaterials absorb up to 80% of incident light. Split ring resonators LC circuits can easily absorb radar and sonar probe beams but can not hide from simple video cameras. However, non metamaterial calcite due to its natural birefringence may render an object appear double. Optofluids allow light energy delivery from roof top to indoors, photobioreactors and photocatalytic systems for lighting and photochemical reactions [David, 2011]. Metamaterials may be used to fabricate stronger small size antennas, WDM detectors for explosives or bio agents, invisible submarines, aircrafts, noise canceling mats, protective devices against earthquake and tsunami, invisibility, universal mirror and many other sizzling science applications. Superabsorber metamaterials may be used to control acoustic, radio and light fields at will [Jing, 2010]. Nanomaterials have long been used in electricity storage. Fuel cells have high energy densities 10^3 Wh/kg but low power densities 10^2 W/kg and capacitors have low energy densities 10^{-2} Wh/Kg but high power densities 10^7 W/Kg. Batteries and supercapacitors fall between them. Lithium metal batteries have 4 to 5 time larger power and energy densities compared to simple lead acid batteries.

Nanoscale materials possess the key to advances in energy conversion and storage, both of which are vital to meet the challenge of global warming and the finite nature of fossil fuels [Antonino, 2006]. Nanomaterials in particular offer unique properties or combinations of properties as electrodes and electrolytes in a range of energy devices. Flexible battery technology allows to store electricity in piece of paper. ZnO modified paper can store electricity. Nanotechnology has developed nanotubes, nanowires and graphemes for thin films, 3D composite structures for electronics and energy applications. Periodic echoes are heard on the possibility of nanowires replacing copper cables. Heat harvesting nano silicon structures can convert heat to electricity but question whether nano structures can bear the burden of GW is still not certain. There is hope that the control, harvesting, and generation of electromagnetic energy through structured manmade materials can solve energy issue. Current research on optenna, rectenna and nantenna using nanotechnology and metamaterials is likely to help lead the scientific community to technology horizon where free optical energy would be available to everyone. DARPA energy harvesting project has reported three layers holy-grail consisting of solar panel, rectenna array and flexible batteries. Solar cells absorb radiation (>1.1eV), rectenna (<1.1eV) and flexible batteries IR. Flexible printable batteries are also being considered for RFID as one charge can go for several hours. Geographical deserted areas bearing oil and gas also have more sunlight than others so they will continue to maintain their energy center positions even after oil depletion.

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